The "Bucket Brigade" Mechanism of Proton Diffusion in Superprotonic Conductors

Proton diffusion plays a central role in many processes ranging from the regulation of biological functions to the production of electricity in fuel cells. The renewed emphasis on developing the next generation of portable sources of power requires the development of lightweight protonic conducting materials for use as electrolytic membranes [1]. Furthermore, understanding the atomic-scale mechanism of protonic diffusion in candidate materials is necessary to optimize their performance. Since neutrons are particularly sensitive to hydrogen, neutron scattering is an extremely valuable probe of proton dynamics (including diffusion). Moreover, because the wavelength of neutrons is comparable to interatomic distances, neutron scattering is capable of revealing the atomic-scale geometry of protonic motions in a way that is unmatched by other spectroscopic probes. Computational techniques also provide detailed atomistic information about proton incorporation and dynamics. Because of the simplicity of the scattering mechanism, computational results can be directly compared to neutron scattering data. Thus neutron scattering and computational methods are a powerful combination for understanding the performance of protonic conducting materials [2]. Here we briefly describe neutron vibrational spectroscopy (NVS) and quasielastic neutron scattering (QNS) measurements on superprotonic conductors of the general formula $MHXO_4$ (M = Rb, Cs, X = S, Se, etc.) that reveal detailed information on the proton-conduction mechanism.

The crystal structure of alkali-metal hydrogen sulfates and selenates consists of chains of XO_4 tetrahedra (Fig. 1), which are linked by hydrogen bonds, O-H··O. Due to the proximity of the proton site to the midpoint of the O-O separation, it is believed that the proton is dynamically disordered, yielding symmetric hydrogen bonds. However, at a sufficiently low temperature, one expects that the protons may order, giving rise to observable changes in the vibrational spectrum. Above room temperature, there is an orientational order-disorder transition to a phase in which the tetrahedra are dynamically disordered and which displays a very large protonic conductivity that should be observable by QNS.

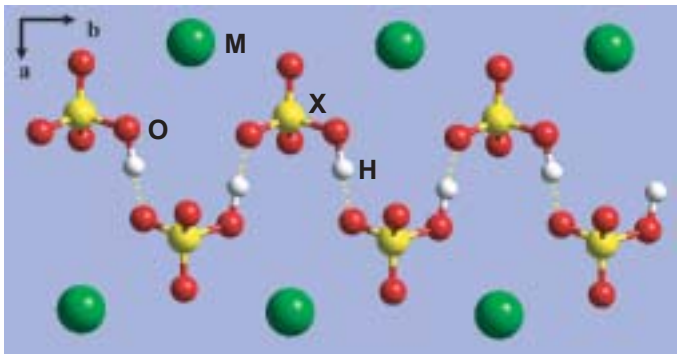

Fig. 1. Projection of the $MHXO_4$ structure, showing the zigzag pattern of the hydrogen bonds between XO_4 tetrahedra. Yellow dashed lines indicate the hydrogen bonds.

Figure 2 summarizes NVS results on $RbHSO_4$ measured using the Filter Analyzer Neutron Spectrometer. At low temperatures, the NVS spectrum shows sharp peaks at 83.3 meV and 99.7 meV. The temperature dependence of these peaks is quite unusual. The intensities decrease very rapidly with increasing temperature and almost disappear at temperatures as low as 200 K. In addition, while the high-energy mode softens, as expected, the low-energy mode hardens by about 2 meV as the temperature is increased. Near 200 K, these two modes collapse to form a broad feature around 95 meV. This suggests that there is significant proton motion even at this low temperature. We believe that this unusual behavior is related to dynamically disordered hydrogen bonds arising from breaking and reforming O-H bonds. Careful neutron diffraction studies in deuterated materials are underway to

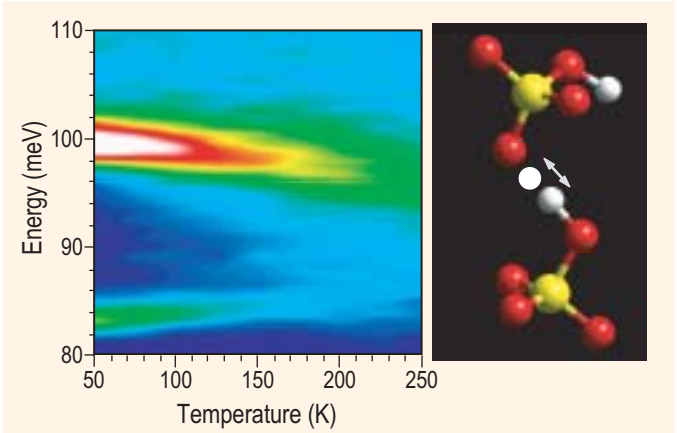

Fig. 2. Temperature-dependent NVS measurements of $RbHSO_4$. As discussed above, these results suggest very large amplitude proton motions are present at temperatures as low as ≈ 100 K. The right panel illustrates the dynamically disordered hydrogen bonding, which is most likely responsible for this unusual temperature dependence.

look for significant changes in the apparent locations or thermal factors of the protons at these temperatures. It should be noted that since this type of dynamical disorder is localized to two neighboring oxygen ions, it cannot be responsible for long-range protonic conduction.

To probe protonic diffusion directly, the temperature dependence of the QNS was measured for $CsH(SO_4)_{1-x}(SeO_4)_x$ ($x \approx 0.24$) above room temperature using the Fermi-Chopper time-of-flight Spectrometer. The data were fit as a function of the scattering vector Q (assuming both elastic and quasielastic components) in order to extract the Elastic Incoherent Structure Factor (EISF), which is defined as the fraction of the total scattering that is elastic. Figure 3 shows the EISF as a function of Q for several different temperatures. The fact that a non-zero EISF is observed even at 475 K indicates that, within the time window of the measurement (< 20 ps), the hydrogen motion is localized rather than diffusive. Moreover, the fact that the EISF changes with temperature indicates the existence of non-energetically equivalent proton-sites. The best fit to the EISF (shown by the solid lines in Fig. 3) was obtained assuming two types of hopping motions for the protons between pairs of inequivalent sites. The agreement between the data and the model is excellent. The two jump distances, 1.4 Å and 4.5 Å, are essentially independent of temperature (see Fig. 4). Looking at the structure, these can easily be identified as the reorientation of the SO_4-H group around the quasi-threefold (1.4 Å) and the quasi-twofold (4.5 Å) axes (Fig. 4). The ratio of the times that the proton spends in each of the two sites depends exponentially on temperature as expected (solid lines in the upper left panel of Fig. 4). For the short-distance reorientation, the time ratio goes rapidly to unity around 405 K, just before the super-protonic phase transition, indicating that the two sites are equally populated. For the long-distance reorientation, the ratio approaches 0.2 at the highest temperature.

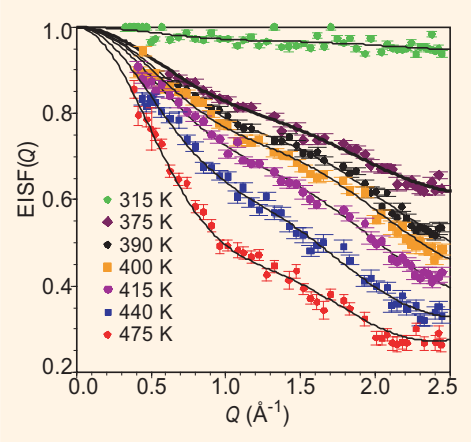

Fig. 3. EISF (dots) and fits (solid lines) at different temperatures for $CsH(SO_4)_{1-x}(SeO_4)_x$ ($x \approx 0.24$).

These findings are consistent with a previous neutron-powder-diffraction study on the high-temperature phase of $CsHSO_4$, which revealed four different orientations of each tetrahedron [3]. Most probably the four orientations mimic the dynamical orientational disorder of the tetrahedra that we observe by QNS. We also note that the two types of dynamic orientational disorder shown in Fig. 4 do not result in long-range protonic conduction since the motions are localized on a single tetrahedron. However, when one combines these two motions with the dynamically disordered hydrogen bond implied by NVS, the mechanism of protonic conduction can be understood. Namely, the protons move between two neighboring tetrahedra via dynamically disordered hydrogen bonds. The tetrahedra then reorient, allowing the protons to move to a third tetrahedron, again via the dynamically disordered hydrogen bonds. Thus the tetrahedra play the role of a "bucket brigade" by accepting a proton from an adjacent tetrahedron then turning and handing it the tetrahedron on the other side. On the atomic scale, superprotonic conductivity occurs in the $MHXO_4$ family of compounds due to this efficient mechanism of transporting protons through the lattice.

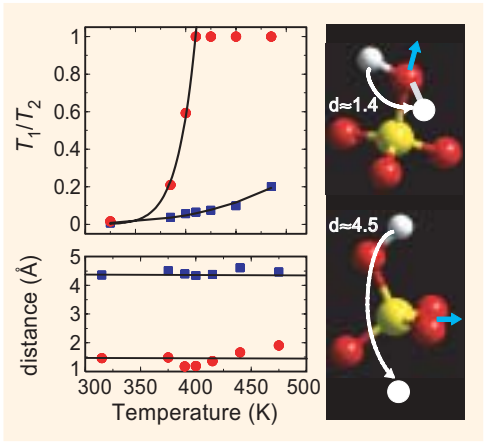

Fig. 4. Top: Temperature dependence of the ratios of the residence times T_1 to T_2 for the pair of two-site hopping motions identified by QNS. Bottom: The two jump distances obtained from QNS as a function of temperature. These distances correspond to the two reorientational motions shown on the right. The red circles correspond to the motion depicted on top while the blue squares correspond to the motion shown on the bottom.

References

[1] *National Hydrogen Energy Roadmap*, DOE, Germantown, MD, 2002.

[2] T. Yildirim, B. Reisner, T. J. Udovic, and D. A. Neumann, Sol. State Ionics **145**, 429 (2001).

[3] A. V. Belushkin, C. J. Carlile, W. I. F. David, I. R. Ibberson, L. A. Shuvalov, W. Zajac, Physica **B174**, 268 (1991).

T. Yildirim, D. A. Neumann, and T. J. Udovic
NIST Center for Neutron Research
National Institute of Standards and Technology
Gaithersburg, MD 20899-8562